MINOR DITERPENOIDS OF Teucrium chamaedrys

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UDC 547.913

Four bitter substances have been obtained previously [1] from Teucrium chamaedrys L., and the structure (I) has been shown for the main component (teucrin A) [2, 3]. We have now isolated another three new minor compounds from this plant, which we have grouped under the general name of teucrins. Their empirical formulas, physical constants, and yields are given in Table 1. Information showing the structures of four of these compounds (teucrins B, E, F, and G) is given in this paper.

Unlike teucrin A, the molecules of the minor diterpenoids each contain 20 carbon atoms. They all belong to the type of rearranged labdanes, have very similar IR and mass spectra, and also include common groupings such as furan and lactone rings, hydroxyls, and secondary methyl groups. In the mass spectra of the teucrins, fragments with m/e 95, 94, and 81 predominate with relative intensities characteristic for the diterpene furolactones picropoline [4] and columbin [5].

Teucrin B (II), according to spectral and chemical results, contains a furan ring, two secondary hydroxyls, and two γ-lactone rings. The latter is confirmed by the consumption of two molar equivalents of alkali by it. Teucrin B does not contain vicinal hydroxyls, since it is not oxidized by sodium periodate. Its acetylation gives an acetate (III) containing no hydroxyls.

The NMR spectrum of this compound (Table 2) shows the signals of two AB protons in the 4.40-ppm region due to the methylene grouping of a lactone located on a completely substituted carbon atom. The singlet of two acetate methyls is also observed. As in the spectrum of teucrin A [2, 3], it contains the signals of a secondary methyl group, of a H_{12} proton in the geminal position to the ester oxygen of the lactone, and the protons of a β-substituted furan.

On the basis of the spectral characteristics and biogenetic relationships of all the teucrins, the following partial distribution of the functional groups in teucrin B may be assumed. One lactone ring is located in the α position to the furan ring, as in teucrin A. The second lactone ring can be formed only if the carbonyl is located at C_4 and its methylene grouping, at C_5; only the C_8 position remains for the methyl group. This is confirmed by the results of a study of the product of the reduction of teucrin B with lithium tetrahydroaluminate (IV) and the acetate (V) of this product. The NMR spectrum of the latter shows a downfield shift of the H_{12} signal. In the 4.0-4.9-ppm region there are the signals of six protons belonging to the three methylene groupings obtained from the reduction of the lactone rings.

To prove the position of the hydroxy groups, teucrin B was oxidized to a diketo derivative (VI), which did not belong to the type of α- or β-diketones or to the β-keto lactones capable of enolization. Hence, the hydroxyls are present in different rings, and, at the same time, neither of them occupies the C_3 position.

In the NMR spectrum of (III) both protons at the acetate groups give signals in the form of multiplets and, consequently, they each interact with more than two other protons. This fact confirms the presence of an acetate group in ring B at C_7 and excludes position C_6. The question was answered, finally, after a comparison of the mass spectra of the diketone (VI) and its deuterated analog. Exchange of deuterium with six hydrogen atoms was found, which shows the location of the hydroxyls at C_1 and C_7.

Teucrin E (VII), on the basis of its IR and NMR spectra and also the results of titration with alkali, contains two γ-lactone groupings, a hydroxyl, a β-substituted furan ring, and a secondary methyl group. It is readily acetylated by acetic anhydride in pyridine, forming a monoacetate (VIII) and is oxidized by

Institute of Chemistry, Academy of Sciences of the Moldavian SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 589-598, September-October, 1974. Original article submitted June 11, 1973.

TABLE 1. Diterpenoids Isolated from Teucrium chamaedrys L.

Substance*	Empirical formula	mp, °C	$[\alpha]_D^{20}$, deg (pyridine)	R_f†	Yield, % on the dry plant
Teucrin A (I)	$C_{19}H_{30}O_6$	251–253	+ 163	0,75	0,14
Teucrin B (II)	$C_{20}H_{24}O_7$	239–241	+ 5,5	0,50	0,0083
Teucrin C	$C_{20}H_{26}O_7$	191–193	+ 4,1	0,45	0,006
Teucrin D	$C_{20}H_{26}O_6$	220–222	+ 19,0	0,40	0,002
Teucrin E (VII)	$C_{20}H_{24}O_6$	235–238	– 25,0 acetone	0,60	0,018
Teucrin F (XII)	$C_{20}H_{22}O_7$	225–230	+ 6,0	0,75	0,007
Teucrin G (XIX)	$C_{20}H_{22}O_8$	245–249	–	0,75	0,003

* The letters by which the teucrins are denoted are given in the order of their isolation from the plant.
† In the system consisting of chloroform with 8% of methanol.

chromium trioxide to a keto derivative (IX), which shows the equatorial orientation of the hydroxyl. Compound (IX), just like (VIII), contains no hydroxy groups. The presence of similar signals in the NMR spectra of the acetates of teucrins B and E gives grounds for considering that these compounds have similar structures. Thus, in the spectrum of (VIII) (see Table 2) there are the same triplet of the H_{12} proton (5.38 ppm) and the same signals of two protons of the AB type due to the methylene grouping of a lactone (4.37 and 4.86 ppm), but there is also a double doublet of the proton at an acetate group at 4.90 ppm that is absent from the spectra of the ketone (IX).

The reduction of teucrin E with lithium tetrahydroaluminate gave a polyol (X), the acetylation of which led to the production of a pentaacetate (XI) containing no hydroxy groups. In the NMR spectrum of the latter, the H_{12} triplet had shifted to 6.08 ppm, and apart from the signals of the five acetate methyls in the 4.1-4.8-ppm region, the overlapping signals of seven protons were observed – from three methylene groupings and the proton at an acetate group. These results also confirm the position of the lactone rings in the molecule of compound (VII).

The position of the hydroxyl at C_6 was established on the basis of the fact that the proton at the acetate group in compound (VII) exists in interaction with two vicinal protons (doublet of doublets in the PMR spectrum) and the ketone exchanges only two hydrogen atoms for deuterium.

The stereochemistry of the linkage of the A/B rings in teucrin E was studied by means of an analysis of the circular dichroism (CD) curve of the keto derivative (IX), which shows a negative Cotton effect (CE) with a distinct fine structure which is characteristic for 6-keto-10β-steroids [6]. The results of a comparison of the signs and amplitudes of the CEs of the ORD and CD curves of some 6-keto derivatives of cholestane, coprostane, clerodin [7], and compound (IX) showed the 5α,10β configuration of the substituents in teucrin E.

The axial orientation of the H_6 proton (equatorial OH) was shown by the value of the chemical shift of the signal in the NMR spectrum of (VIII), and also by the overall constant of its interaction with the two H_7 protons, $J_{aa} + J_{ae} = 15.0$ Hz.

The α orientation of the substituent at C_5, according to the possibility of the existence of the lactone ring, involves the analogous α direction of the substituent at C_4. It follows from the facts given that the structure and absolute configuration of teucrin E must be expressed by formula (VII).

Teucrin F (XII), a compound difficult to separate chromatographically from teucrin A, also contains two γ-lactone rings, a furan ring, hydroxyls, and a secondary methyl group. Its acetylation with acetic anhydride in pyridine led to the formation of the monoacetate (XIII), and oxidation with chromium trioxide in pyridine to the keto derivative (XIV). Both these compounds contain hydroxy groups. On acetylation under more severe conditions – boiling in acetic anhydride with sodium acetate – compound (XIII) yielded a diacetate (XV), and the ketone (XIV) yielded the enol acetate (XVI). This shows the presence in the molecule of (XII) of secondary and tertiary hydroxyls, and since teucrin F is not oxidized by sodium periodate, these are not in the vicinal position to one another.

TABLE 2. Chemical Shifts (ppm) and Spin–Spin Coupling Constants (Hz) of the Protons of Derivatives of the Minor Teucrins

Constant	H_1	H_3	H_9	H_6	H_7	H_{11}	H_{12}	H_{13}, H_{14}, H_{15}	$2H_{18}$	H_2	Other protons
III	5,15*	—	—	—	4,90 m	—	5,29 t J‡ =17,0	6,35; 7,48; 7,60	4,50/4,32 AE J =10,5	0,90 d J=6,0	$2CH_3CO$: 1,98 s
V	5,32 m	—	—	—	5,32 m	—	6,22 t J‡ =17,0	6,60; 7,50; 7,80	4,00–4,90	0,75 d J =6,0	$6CH_3CO$: 1,95–2,02 $2H_{17}$, $2H_{19}$: 4,00–4,90
VIII	—	—	—	4,90 dd J*=15,5	—	—	5,38 t J‡ =17,0	6,48; 7,54; 7,68	4,86/4,37 AB J =11,0	0,90 d J 6,0	CH_3CO : 1,94 s
IX† $CHCl_3$	—	—	—	—	—	—	5,22 t J ‡ =17,0	6,33; 7,45;	4,85/4,28 AB J—10,5	1,10 d J=6,5	—
XI	—	—	—	4,10–4,80	—	—	6,08 dd J ‡ =12,0	6,52; 7,48; 7,72	4,10–4,80	0,63 d J=6,0	$5CH_3CO$: 1,88–2,04 $2H_{17}$, $2H_{19}$: 4,10–4,80
XIII† $CDCl_3$	—	6,00 m	5,20–5,60	—	5,20–5,60	—	5,20–5,60	6,32; 7,39;	4,40/4,05 AB J–12,0	0,95 d J =6,0	CH_3CO : 1,95 s
XV	2,57; 1,88	6,04 oct	5,58 dd $J_{3,2}$=9,0	—	5,49 $W_{1/2}$=8,0	3,00 dd J‡ =5,0+ +12,0	5,41 t J ‡ =17,0	6,45; 7,50; 7,74	4,62/4,18 AB J—11,0	0,85 d J=6,5	$2CH_3CO$: 2,00; 1,98 s
XVI	—	6,08	5,53 d J = 3,5	6,14 s	—	3,35 дд. J ‡ =5,0+ +12,0	5,45 dd J ‡ =16,5	6,48; 7,53; 7,70	4,86/4,32 AB J=10,5	1,04 d J=6,0	$2CH_3CO$: 2,03; 1,96 s

* s – singlet; d – doublet; t – triplet; dd – doublet of doublets; m – multiplet; oct – octet. The spectra were taken in deuteropyridine at a frequency of 100 MHz.

† Spectrum taken at a frequency of 60 MHz.

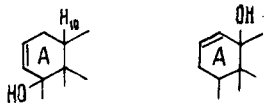
‡ Sum of the coupling constants.

From the elementary analysis and the functional composition of teucrin F given above it follows that its molecule contains one double bond; the secondary hydroxyl is not in the α position to this, since the UV spectra of compounds (XIV) and (XVI) lack absorption apart from the furan absorption. A confirmation of this is given by the NMR spectra of the monoacetate (XIII) and the diacetate (XV) (see Table 2).

The tertiary nature of the hydroxyl in the monoacetate (XIII) is shown by the fact that in the NMR spectra of the diacetate there are no downfield signals whatever in comparison with the spectrum of (XIII). In the spectrum of (XV) the signals of two protons of the AB type (4.62 and 4.18 ppm) corresponding to an isolated methylene grouping are clearly seen. As in the case of teucrins B and E, the latter is part of a lactone ring formed by substituents at C_4 and C_5.

The use of the INDOR method in the spectrum of the diacetate (XV) showed the presence in teucrin F of the fragment $\diagdown CH{=}CH{-}CH_2{-}\overset{\diagup}{C}H$, which can be present only in ring A. Thus, the coupling of two olefinic protons (J = 9.0 Hz) at 6.04 ppm (octet) and 5.58 ppm (doublet of doublets) is observed. The proton at 6.04 ppm also couples with the two methylene protons at 2.57 ppm (J = 10.0 Hz) and 1.88 ppm (J = 2.5 Hz). The methine proton at 3.09 ppm also interacts with the latter protons (doublet of doublets, J = 5.0 + 12.0 Hz). The remaining signals in the weak field of the spectrum at 5.41 and 5.49 ppm belong to the H_{12} atom present in the lactone ring and the proton at the secondary acetate group, respectively.

On the basis of the NMR spectra, the structure of ring A can be expressed by either of the fragments a and b.



a b

The choice in favor of structure a was made on the basis of the following transformation. On reduction by lithium tetrahydroaluminate, teucrin F gives a hexaol (XVII), which is oxidized by sodium periodate to the nor derivative (XVIII) containing, according to IR and UV spectroscopy, an α,β-unsaturated ketone.

It follows from what has been said that the lactone ring can be constructed in two ways: either the carbonyl is located at C_4 and the CH_2O grouping at C_5, or conversely. Since compounds (XIII) and (XIV) are incapable of being dehydrated by thionyl chloride in pyridine, the first variant must be the true one.

The position of the secondary hydroxyl in teucrin F follows from the NMR spectrum of the enol acetate (XVI), which differs from the spectrum of (XV) by several features. The doublet of the methyl group is shifted downfield by 0.19 ppm – the characteristic shift of an allyl methyl group. The signal of the proton that appears in the spectrum of (XV) at 5.49 ppm is absent. In place of it a sharp singlet belonging to the olefinic proton of an enol acetate group has appeared at 6.14 ppm. In the 5.35-5.65-ppm interval the signals of the H_{12} and H_3 protons (doublet of doublets at 5.45 ppm and doublet at 5.53 ppm, respectively) have remained. The singlet nature of the enolic proton shows that it is located at C_6, and not C_7, since in the latter case it would show additional coupling with H_8. Consequently, the keto group in (XIV), and therefore the secondary hydroxyl in teucrin F, is located at C_7.

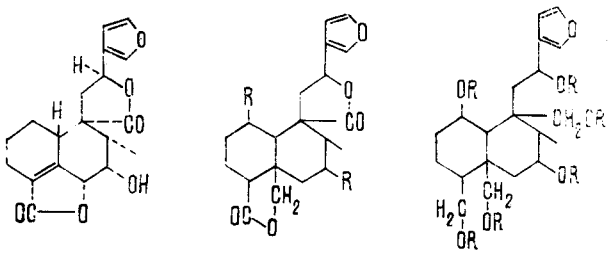
The stereochemistry of teucrin F was elucidated as the result of an analysis of the ORD curve of the ketone (XIV). Its sign and amplitude correspond to the analogous curve of ketosolidagonic acid [8], which has the trans-A/B-10β configuration. The axial direction of the H_{10} proton (J = 5.0 + 12.0 Hz) also follows from the NMR spectra. The existence of a lactone ring is possible only in the case of the equatorial direction of the $C_4{-}C{=}O$ bond and the axial direction of the tertiary hydroxyl. According to the chemical shift and the half-width of its signal ($W_{1/2}$ = 8.0 Hz) in the NMR spectrum of (XV) [9], the H_7 proton occupies the equatorial position.

The absolute configuration of teucrin F at the asymmetric centers considered is expressed by formula (XII).

Teucrin G (XIX) was isolated as a satellite of teucrin F, from which it differs only by an atom of oxygen in the molecule. The structure (XIX) is proposed for it on the basis of its chemical transformations which take place similarly to those of teucrin F. Teucrin G contains, according to its chemical and

spectral characteristics, a furan ring, two γ-lactone rings, and secondary and tertiary hydroxyls. The compound is not oxidized by sodium periodate. Like teucrin F, it forms a monoacetate (XX) and a keto derivative (XXI) which, on severe acetylation, give the diacetate (XXII) and the enol acetate (XXIII), respectively. The derivatives (XX) and (XXI) are not dehydrated by thionyl chloride in pyridine. In view of the fact, also, that the IR spectra of teucrins F and G and their derivatives are very similar, it can be stated that teucrin G is the 2,3-epoxy derivative of teucrin F.

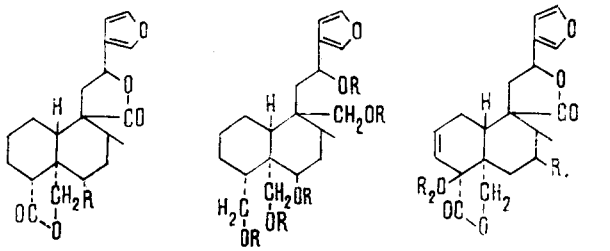
The question of the structures of the two other teucrins, C and D, is being studied.



I

II, III, VI

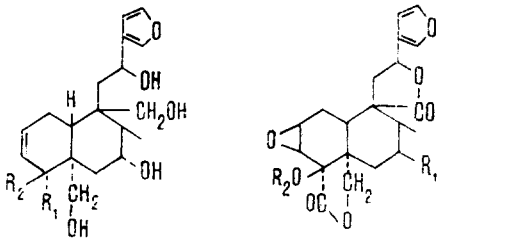
IV, V



VII – IX

X, XI

XII – XVI



XVII, XVIII

XIX – XXIII

II. R=OH; III. R=OAc; IV. R=H; V. R=Ac; VI. R= =O; VII. R=α-OH; VIII. R= =α-OAc; IX. R= =O; X. R=H; XI. R=Ac; XII. R_1=α-OH, R_2=H; XIII. R_1=α-OAc, R_2=H; XIV. R_1= =O, R_2=H; XV. R_1=α-OAc, R_2=Ac; XVI. R_1=OAc, R_2=Ac, Δ; XVII. R_1=CH_2OH, R_2=OH; XVIII. R_1+R_2= =O; XIX. R_1=OH, R_2=H; XX. R_1=OAc, R_2=H; XXI. R_1=OAc, R_2=Ac; XXIII. R_1=OAc, Δ, R_2=Ac.

EXPERIMENTAL

The CD and ORD curves were taken on a Spectropol spectropolarimeter (V. A. Babkin, Institute of Organic Chemistry, Novosibirsk); the IR spectra on a UR-10 spectrometer in chloroform; the UV spectra on a Specord UV-Vis spectrometer in ethanol; the NMR spectra on an HA-Varian-100 instrument in deuteropyridine (with tetramethylsilane as internal standard); and the mass spectra on an MKh-1303 instrument at 140°C with an ionization energy of 70 eV. The values of $[\alpha]_D$ were determined on a Zeiss instrument in pyridine, and the melting points on a Koffler block. Silica gel in fixed and nonfixed layers was used as the adsorbent for TLC.

General methods are given for the monotypical reactions with indications of the yield of each individual substance. The analyses of all the compounds corresponded to the calculated figures.

Isolation of Teucrins E, F and G. Teucrins E, F, and G, just as teucrins A, B, C, and D, were isolated from an acetone extract of the plant in the manner described previously [1]. The chloroform fraction, after the elimination of flavonoid substances with 2% alkali, was chromatographed on a 50-fold amount of silica gel. Elution was performed with chloroform containing 2% of methanol, giving a crystalline mixture of teucrins A, F, and G, and with chloroform containing 3% of methanol, giving a fraction from which,

after rechromatography and crystallization, teucrin E was isolated in a yield of 0.018% of the weight of the dry plant. The mixture of teucrins A, F, and G was separated into its individual components by repeated chromatography on silica gel in benzene containing from 15 to 20% of acetone. The yields of teucrins F and G amounted to 0.007 and 0.003%, respectively, of the weight of the dry plant (VII).

Teucrin E, $C_{20}H_{24}O_6$, mp 235-238°C (from acetone–ether). IR spectrum (KBr), cm^{-1}: 3460, 3155, 1765, 1750, 1600, 1505, 1185, 1022, 880; UV spectrum: λ_{max} 211 nm (ε 5900); M^+ 360.

Teucrin F, $C_{20}H_{22}O_7$, (XII), mp 225-230°C (from methanol–chloroform–ether). IR spectrum (KBr), cm^{-1}: 3420, 3150, 1780, 1752, 1600, 1508, 1180, 1165, 1030, 880; UV spectrum: λ_{max} 209 nm (ε 5500); M^+ 374.

Teucrin G, $C_{20}H_{22}O_8$, (XIX), mp 245-249°C (from methanol–chloroform–ether). IR spectrum (KBr), cm^{-1}: 3425, 3150, 1780, 1755, 1600, 1505, 1185, 1025, 880. UV spectrum: λ_{max} 210.5 nm (ε 6500); M^+ 390.

Acetylation of Teucrins B, E, F, and G. To a solution of 50 mg of the appropriate substance in 1 ml of pyridine was added 0.5 ml of acetic anhydride, and the mixture was left at room temperature for two days. After the usual working up, extraction with chloroform, and chromatography of the crude product on silica gel, the corresponding acetate (III, VIII, XIII, or XX) was isolated.

The Amorphous Substance (III) (45 mg), $C_{24}H_{28}O_9$, IR spectrum, cm^{-1}: 1775, 1760, 1740, 1600, 1508, 1240, 880.

Compound (VIII) (40 mg), $C_{22}H_{26}O_7$, mp 232-234°C (chloroform–ether). IR spectrum, cm^{-1}: 1760, 1740, 1510, 1240, 1115, 880.

Substance (XIII) (42 mg), $C_{22}H_{24}O_8$, mp 225-227°C (chloroform–ether). IR spectrum, cm^{-1}: 3555, 1782, 1760, 1738, 1600, 1506, 1250, 1170, 880.

The Acetate (XX), $C_{22}H_{24}O_9$, was obtained in the form of a vitreous mass (45 mg). IR spectrum cm^{-1}: 3580, 1780, 1768, 1740, 1600, 1506, 1252, 1185, 1170, 880, 860.

Oxidation of Teucrins B, E, F, and G. To a complex of 200 mg of chromium trioxide in pyridine was added a solution of 80 mg of the appropriate substance in 0.5 ml of pyridine, and the mixture was left at room temperature for 24 h. After the usual working up and chromatography on silica gel with elution by chloroform and a mixture of chloroform with 2% of methanol, the corresponding ketone was isolated in each case.

The Diketone (VI) (60 mg), $C_{20}H_{20}O_7$, mp 272-274°C (acetone–ether). IR spectrum (KBr) cm^{-1}: 3160, 1780, 1760, 1725, 1710, 1600, 1510, 1190, 1025, 880. UV spectrum: λ_{max} 210.5 nm (ε 9200); M^+ 372.

Mixture of 25 mg of the Initial Alcohol (VII) and 25 mg of the Ketone (IX), $C_{20}H_{22}O_6$, mp 200-202°C (chloroform–ether). IR spectrum, cm^{-1}: 1780, 1768, 1716, 1600, 1510, 1185, 1020, 880. CD, λ, nm (Δε): 330 (0), 309 (−1.60), 300 (−2.25), 295 (−2.00), 291 (−2.12), 255 (0) (C 0.0028, dioxane); M^+ 358.

Compound (XIV) (55 mg), $C_{20}H_{20}O_7$, mp 235-238°C (chloroform). IR spectrum (KBr), cm^{-1}: 3500, 3160, 1785, 1752, 1600, 1508, 1190, 1180, 1140, 1020, 880. UV spectrum: λ_{max} 209 nm (ε 6800). ORD: $[\alpha]_{241}$ −1041°, $[\alpha]_{243}$ −1280°, $[\alpha]_{257}$ 0°, $[\alpha]_{265}$ +452°, $[\alpha]_{278}$ +591°, $[\alpha]_{300}$ 0°, $[\alpha]_{318}$ −510°, $[\alpha]_{330}$ −240°, $[\alpha]_{350}$ −87° (c 0.092; dioxane). M^+ 372.

Substance (XXI) (55 mg), $C_{20}H_{20}O_8$, mp 257-260°C (chloroform–ether). IR spectrum (KBr), cm^{-1}: 3465, 3160, 1780, 1756, 1700, 1600, 1506, 1190, 1145, 1025, 880, and 850. UV spectrum: λ_{max} 210 nm (ε 5600). M^+ 388.

Deuteration of the Ketones (VI) and (IX). To a solution of 15 mg of the appropriate substance in 0.4 ml of absolute dioxane was added 0.15 ml of deuterium oxide and 10 ml of anhydrous calcined sodium carbonate, and the mixture was left at room temperature for 36 h. Then it was filtered and the filtrate was acidified with dilute hydrochloric acid and extracted with chloroform. The extracts were washed with water to neutrality, dried, and evaporated. This operation was performed three times. The substance obtained from the diketone (VI) had the composition $C_{20}H_{14}D_6O_7$ (12 mg), mp 272-274°C, M^+ (main peak) 378; the substance obtained from the ketone (IX) had the composition $C_{20}H_{20}D_2O_6$ (13 mg), mp 199-202°C, M^+ (main peak) 360.

Preparation of Compounds (XV), (XVI), (XXII), and (XXIII). A mixture of 50 mg of one of the initial compounds (XIII), (XIV), (XX), and (XXI), 1.5 ml of acetic anhydride, and 150 mg of fused sodium acetate

was boiled under reflux for 6 h. The cooled solution was diluted with water and extracted with chloroform. The extracts were washed with sodium bicarbonate solution and with water, dried, and evaporated. The residue after chromatography on silica gel in chloroform yielded the corresponding derivative.

The Diacetate (XV) (40 mg), $C_{24}H_{26}O_9$, mp 226-229°C (chloroform–ether). IR spectrum, cm^{-1}: 1788, 1755 (very strong), 1600, 1505, 1250, 880; UV spectrum: λ_{max} 210 nm (ε 8000).

The Enol Acetate (XVI) (35 mg), $C_{24}H_{24}O_9$, mp 190-192°C (chloroform–ether). IR spectrum, cm^{-1}: 1785, 1763 (very strong), 1600, 1505, 1235, 1165 (very strong), 878; UV spectrum: λ_{max} 206 nm (ε 9800).

The Diacetate (XXII) (42 mg), $C_{24}H_{26}O_{10}$, in the form of an amorphous mass. IR spectrum, cm^{-1}: 1785, 1753 (very strong), 1600, 1505, 1250, 880; UV spectrum: λ_{max} 209 nm (ε 7200).

The Amorphous Enol Acetate (XXIII) (38 mg), $C_{24}H_{24}O_{10}$. IR spectrum, cm^{-1}: 1795, 1765 (very strong), 1600, 1505, 1160, 880, 865; UV spectrum: λ_{max} 208 nm (ε 9500).

Under these conditions, the ketone (IX) underwent no change.

Reduction of Teucrins B, E, and F, and Production of the Acetates (V) and (XI). Over 3 h, a solution of 100 mg of the appropriate substance in tetrahydrofuran was added to a boiling solution of 200 mg of lithium tetrahydroaluminate in tetrahydrofuran, and then the mixture was heated for another 12 h. After cooling, the excess of reagent was destroyed, and the mixture was acidified with sulfuric acid to pH 3 and extracted with butanol. The extracts were washed with water to neutrality, dried, and evaporated in vacuum. The residue was chromatographed in 4 g of silica gel. Mixtures of chloroform with 5-8% of methanol eluted the corresponding polyhydroxy compounds in the form of viscous liquids:

(IV), 75 mg. IR spectrum (KBr), cm^{-1}: 3420, 1600, 1507, 1010, 1040, 880.

(X), 80 mg. IR spectrum (KBr), cm^{-1}: 3400, 1600, 1505, 1030, 880.

(XVII), 70 mg. IR spectrum (KBr), cm^{-1}: 3425, 1510, 1165, 1030, 880; UV spectrum: λ_{max} 211 nm (ε 9100).

Compounds (IV) and (X) after acetylation in the usual way with acetic anhydride in pyridine gave amorphous acetates:

(V), 80 mg. $C_{32}H_{44}O_{13}$. IR spectrum, cm^{-1}: 1730, 1595, 1500, 1252, 1030, 880.

(XI), 75 mg. $C_{30}H_{42}O_{11}$. IR spectrum, cm^{-1}: 1730, 1720, 1245, 1030, 880.

Oxidation of Compound (XVII). To a solution of 60 mg of substance (XVII) in a mixture of 0.6 ml of water and 0.2 ml of methanol was added 80 mg of sodium metaperiodate in aqueous methanol. After standing for 12 h, the mixture was diluted with water and extracted with chloroform. The extracts were washed with water and dried. The residues, after purification by chromatography on silica gel (3 g), yielded 40 mg of a vitreous substance (XVIII) with the composition $C_{19}H_{26}O_6$. UV spectrum: λ_{max} 217 nm (ε 7400), 227 nm (ε 12,000). IR spectrum (KBr), cm^{-1}: 3500, 3150, 1665, 1635, 1511, 1165, 879.

SUMMARY

The structures of four new diternenoids of Teucrium chamaedrys L.– teucrins B, E, F, and G, belonging to the group of rearranged labdanes – has been shown. For teucrins E and F, the trans-(5α, 10β)-linkage of rings A/B has been shown.

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